

QUANTIFICATION OF PHASE FRACTION AND AMORPHOUS CONTENT

While many methods can be used to determine the elemental composition of a material, diffraction is one of the few techniques that is also sensitive to the physical arrangement of atoms and molecules in the solid state. Even phases with the same chemical composition, such as graphite and diamond, have different diffraction patterns, dictated by the particular structure of each substance. The diffraction pattern from a mixture is the weighted sum of the patterns from each phase that is present, making it possible for quantitative phase composition to be determined. Prior to the application of Rietveld refinement techniques to the problem of quantitative phase analysis, these measurements required difficult calibrations and were often imprecise. However, Rietveld analysis involves the fitting of the entire diffraction pattern of each component phase based upon a structural model of the material and no standards or prior calibration is required. It should be noted though that even Rietveld analysis could not be used directly to quantify materials with unknown structures or amorphous phases, since such materials cannot be modeled crystallographically. An example where quantitative phase analysis explains the inevitable failure of ceramic thermal barrier coatings was presented in the 1998 NCNR Annual Report.

NIST participation in a round robin on determination of quantitative phase abundance, sponsored by the International Union of Crystallography Commission on Powder Diffraction, provided an excellent opportunity to demonstrate the high quality of data obtained using the 32-detector NCNR high-resolution powder diffractometer at BT-1. The NCNR implementation of the Rietveld technique for phase quantification was found to give excellent agreement with the nominal compositions. In addition, a new method for determining the amorphous phase content of a mixed-phase sample without sample adulteration was validated.

Data were collected using a Cu(311) monochromator ($\lambda = 1.5402 \text{ \AA}$) and 15° incident collimation, and were then processed in the usual procedure to obtain a pseudo-single detector data set. The phase fractions were determined using standard Rietveld refinement techniques, including full refinement of crystallographic and instrumental parameters, as implemented by the GSAS suite of programs. Results for a sample consisting of nearly equal mass fractions of Al_2O_3 , CaF_2 , and ZnO , along with values reported by the other round-robin participants, are given in Table 1; the results obtained at NIST for all other samples are reported in Table 2 along with the nominal phase content. It can be seen from Table

Table 1. Mass fractions (%) of three-phase mixture reported by round robin participants. The ranges are reported for 111 x-ray determinations, 7 neutron determinations, and 4 synchrotron determinations. Standard uncertainties are reported in parentheses for the XRF (x-ray fluorescence, 3 determinations as reported by the organizers) and NIST results (determined from the least-squares refinement).

Phase	Weighed	XRF	x-ray	Neutron	Synchrotron	NIST
Al_2O_3	31.4	31.7(1)	22-49	29-32	31-35	31.7(1)
CaF_2	34.4	33.9(1)	19-42	32-39	34-35	33.9(1)
ZnO	34.2	34.0(1)	25-42	32-35	29-35	34.4(1)

1 that neutron data give significantly more accurate results than synchrotron or laboratory x-ray data, and that the results obtained at NIST are exceedingly good. The high accuracy of these results can be attributed to the intrinsic Gaussian line shape of the reactor neutron source, as well as to the lack of microabsorption and preferred orientation effects that frequently plague x-ray data but are normally negligible with neutron data. The data presented in Table 2 further confirm this conclusion, in that the results for sample 2 (preferred orientation), sample 3 (amorphous content) and sample 4 (microabsorption) all agree well with the nominal phase content.

The determination of amorphous content in a crystalline sample has traditionally involved integration of the area under the broad amorphous hump, giving the relative intensity compared with that of the Bragg scattering. However, in multiphase samples this technique is impractical. An alternative approach is to add a known quantity of a material as an internal intensity standard.

The unique properties of neutron diffraction suggested an alternative approach. Since absorption is negligible for most elements, and since the entire sample is irradiated in the neutron beam, a strategy based on absolute scattering intensities using an external standard was devised.

In the Rietveld technique, the mass of each crystalline phase, w_i , is proportional to the product of the scale factor for that phase, S_i , and the molecular weight of the unit cell contents ($Z_i M_i$) where Z_i is the number of formula units per unit cell and M_i is the molecular weight. Thus for a crystalline multiphase sample of mass w_c ($w_c = \sum w_i$) the relation $w_c \propto \sum S_i Z_i M_i$ is true. The proportionality constant can be determined using mass w_{std} of a completely crystalline known standard under identical data collection conditions, so the relation $w_c/w_{\text{std}} = (\sum S_i Z_i M_i)/(S_{\text{std}} Z_{\text{std}} M_{\text{std}})$ can be used. If the sample mass, w_s ,

Table 2. Comparison of nominal phase composition (%) with that obtained at NIST. The weighed and XRF values were provided by the round robin organizers. Standard uncertainties for the NIST results are given in parentheses.

Sample	Component	Mass fraction weighed	Mass fraction XRF	Mass fraction NIST
1a	Al ₂ O ₃	1.2	1.2	1.3(1)
	CaF ₂	94.8	94.1	94.8(3)
	ZnO	4.0	4.1	3.9(1)
1b	Al ₂ O ₃	94.3	94.7	94.4(3)
	CaF ₂	4.3	4.3	4.2(1)
	ZnO	1.4	1.4	1.4(1)
1c	Al ₂ O ₃	5.0	5.1	4.9(1)
	CaF ₂	1.4	1.3	1.4(1)
	ZnO	93.6	93.2	93.8(3)
1d	Al ₂ O ₃	13.5	13.8	13.7(1)
	CaF ₂	53.6	53.0	53.0(2)
	ZnO	32.9	33.0	33.3(1)
1e	Al ₂ O ₃	55.1	55.8	55.4(2)
	CaF ₂	29.6	29.4	29.2(1)
	ZnO	15.3	15.3	15.4(1)
1f	Al ₂ O ₃	27.1	27.3	26.7(1)
	CaF ₂	17.7	17.4	17.5(1)
	ZnO	55.2	54.9	55.8(2)
2	Al ₂ O ₃	21.3	20.9	21.9(4)
	CaF ₂	22.5	24.1	22.0(4)
	ZnO	19.9	19.5	19.1(6)
	Mg(OH) ₂	36.3	36.1	37.0(3)
3	Amorphous	29.5	27.1	32.3(6)
	Al ₂ O ₃	30.8	31.1	30.7(6)
	CaF ₂	20.1	19.9	18.7(3)
	ZnO	19.7	19.6	18.3(3)
4	Al ₂ O ₃	50.5	50.4	50.5(3)
	Fe ₃ O ₄	19.6	19.6	20.3(2)
	ZrSiO ₄	29.9	29.5	29.3(4)

also contains an amorphous component, w_A , then since $w_A = w_S - w_C$ and the amorphous fraction $f_A = w_A / w_S$, then

$$f_A = 1 - \frac{\sum S_i Z_i M_i}{S_{\text{std}} Z_{\text{std}} M_{\text{std}}} \cdot \frac{w_{\text{std}}}{w_S}$$

Using the GSAS suite of programs, the values for S_i may be obtained from the product of the overall scale factor and the “phase fraction,” or by fixing the overall scale factor to 1.0 so that the refined “phase fractions” are in fact the Rietveld scale factors for each phase.

In order to make sure that data on the unknown and standard materials were collected under identical conditions the automated sample changer was used, the sample volume was reduced to ensure

complete sample irradiation, and identical data collection parameters were employed. In this way, data on any number of unknowns could be compared to a single standard sample since no changes were made to the experimental conditions. An additional benefit was that no adulteration or mixing of the samples was necessary. This technique was used with several single-phase samples in order to compare the crystallinity of potential standards as well as of the unknown samples. In fact, the round robin organizers subsequently sent samples of each of the unmixed phases to NIST for analysis. The results obtained for the round robin sample with amorphous content gave excellent agreement with the mass fractions determined by weighing (see Table 2); the slightly higher amorphous content obtained using the neutron Rietveld technique is explained by the presence of a small amount (1 % to 2 %) of amorphous material in the component crystalline phases.

This external standard technique to determine amorphous content could also be used to determine the mass fraction of a crystalline phase with an unknown structure. For both applications, however, obtaining the best results depends upon obtaining the best diffraction data. The unique capabilities of the NCNR high-resolution diffractometer at BT-1 make this possible; these are summarized below.

FEATURES OF THE BT-1 DIFFRACTOMETER

Automatic six-carousel locking sample changer (vanadium sample cans), ideal sample size: 10 cm³.

Maximum beam size: 15 mm width by 50 mm height.

Collimations: 15' or 7' before monochromator, 20' before sample [30' for Si(531)], 7' before detectors.

Detectors: 32 ³He-filled detectors at 5° intervals; 13° scan range covering 2θ from 0° to 167°.

Monochromators:

Monochromator crystal and Bragg plane	In-pile Collimation angle (°)	Monochromator 2 θ (°)	Relative Bragg Intensities	Flux (neutrons s ⁻¹ cm ⁻²)	Wavelength (Å)	Typical run times (h)
Ge(311)	15	75	3.34	700 000	2.0784	0.5-5
Ge(311)	7	75	1.84	400 000	2.0795	
Cu(311)	15	90	1.00	400 000	1.5401	3-12
Cu(311)	7	90	0.59	200 000	1.5405	
Si(531)	15	120	0.47	200 000	1.5903	6-24
Si(531)	7	120	0.33	100 000	1.5904	